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RHENIUM (AND MASURIUM)

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DEPARTMENT OF COMMERCE - BUREAU OF MINES

RHENIUM (AND MASURIUM)[1]

By Paul M. Tyler[2]

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INTRODUCTION

Masurium and rhenium are two elements known only to a few scientists and known to them for scarcely more than five years. The existence of two members of the manganese family was long suspected, and places were left for them in the orderly table of the periodic system as developed by Mendeljeeff. The empty spaces left in this table some 60 years ago were for elements numbered 43 and 75, respectively, and since it was evident these were related to manganese they were sought for in research laboratories under the names of ekamanganese and dvimanganese. This nomenclature is in harmony with that usually employed in describing hypothetical elements, and the prefixes are taken descriptively from ancient Sanskrit wherein the word "eka" means one and "dvi" (also spelled dui or dwi) means two. Ekamanganese or element 43 was once removed and dvimanganese or element 75 was twice removed from manganese.

It was further possible to predict that these elusive elements would not only be related to manganese but would have a great deal in common with certain other elements. It was reasonable to suppose that element 43, merely because it stood in numerical sequence between element 42 and element 44, would likewise prove to be intermediate in many other respects. Since its next neighbors were molybdenum (No. 42) on the one hand and ruthenium

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[1] - The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6475."

[2] - Chief engineer, rare metals and nonmetals division, U. S. Bureau of Mines.

(No. 44) on the other, ekamanganese could be given in advance what would correspond among persons to a social and economic rating. Similarly, the properties of dvimanganese were likely to be in simple harmony with those of tungsten and with those of osmium, which latter, like ruthenium, is a member of the platinum group of metals.

Another inference, although one which could not be stated with scientific certainty, is that these new elements because they have odd instead of even atomic numbers, would be even more sparingly distributed than their near neighbors, none of which is abundant in nature. This inference has been amply supported by available evidence. These elements eluded discovery until 1925 and never have been found except as minute traces in complex association with relatively rare minerals. In 1930, for the first time, rhenium became available in quantities which give promise of commercial possibilities, but masurium still stands on the border of the unknown, like some distant star speck photographed and identified by vigilant astronomers but invisible without the aid of the powerful tools of science. The telltale flame of element 43 has been charted by its spectrum lines; but beyond that, little more can be said except perhaps to repeat the forecasts made for ekamanganese before the Noddacks captured it and gave it a definite name. Certain rare-mineral dealers will furnish molybdenite samples from Norway which are said to contain masurium as well as rhenium, but except for a few highly technical statements as to its behavior in the spectrograph, nothing in the way of concrete information on masurium has come to the notice of the present writer.

The literature of rhenium is a little less meager and a brief résumé of the data available in the files of the Bureau of Mines may be of interest not merely because of the novelty of the metal but because its unique properties and increasing availability afford a prospect of its finding employment in industry.

RHENIUM

Description and Properties

Rhenium has been isolated as a loose black powder containing more or less hydrogen. This powder, when heated, can be compressed into sticks or bars having considerable strength, much in the same manner as tungsten metal powder is formed into briquettes. When melted in the electric arc the metal is silver-white and exhibits a bright surface resembling platinum and stable in air. Rhenium is the least fusible of all metals, except perhaps tungsten. Some authorities place the melting point at about 3,000° C. or intermediately between the melting points of tungsten and osmium; but others, including one of the discoverers,[3] believe that it may be higher even that that of tungsten and thus exceeded among known elements only by carbon. There are indications that its boiling point is above that of either tungsten or carbon. The metal is exceptionally hard and is quite strong. The density of the black powder (formed by the reduction of the disulphide with hydrogen) is 10.4 but the fused metal is much heavier, having a density of about 20,[4] exceeding gold and tungsten and approaching platinum in this respect.

The specific heat, 0 to 20°, is 0.0346, which is rather low. The figure accepted by the German Atomic Weight Commission for the atomic weight is 188.7 (±0.25), determined

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[3] - Noddack, Ida, Some Physical Constants of Rhenium: Ztschr. Elektrochem., vol. 34, 1928, pp. 629-31; Chem. Abs., vol. 23, April 10, 1929, p. 1537.

[4] - Ibid.

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by Noddack by the reduction of the disulphide in a stream of hydrogen at about 1,000° C. Hönigschmid and Sachtleben,[5] subsequently have recommended 186.31 (±0.02) based upon determinations employing silver perrhenate. The spark and arc spectra are both well known, and several hundred lines in them are known to belong to rhenium. A spectrogram and table of wave lengths of the lines of the L-series of the Roentgen spectrum, as determined by Beuthe, are published in a German journal.[6] The ultimate lines of the optical spectrum, especially the triplet at 3,640 A. U. are of special importance, as they serve to detect the presence of the elements in concentrations down to 1 part in 10,000,000. The Bureau of Standards has recently been investigating the spectrum of rhenium, and a preliminary report appears in its Technical News Bulletin (No. 166) for February, 1931. The electrical conductivity, atomic heat, and other physical properties of the metal have been investigated, but the figures obtained are not available. Platinum filaments heated in the chloride, $ReCl_6$, become plated with rhenium.

Chemically rhenium resembles manganese. It forms a yellow heptoxide, Re_2O_7, which dissolves freely in water and alcohol and which is sufficiently acid in water solution to dissolve zinc and iron with evolution of hydrogen. This acid is considered to have the formula $HReO_4$ and to be analagous to $HMnO_4$, forming potassium perrhenate, ($KReO_4$) and other perrhenates, including those of sodium, ammonium, caesium, silver, calcium, barium, and neodymium. Unlike permanganates, all these salts are colorless (at least as regards the acid radical) but like permanganates they are more or less freely soluble in water, except for the silver salt which is only slightly soluble. The alkali salts can be melted in air without decomposition and the slightly acid solutions are not affected by weak reducing agents, but when treated with stronger reducing agents they acquire a yellow color, and a concentrated solution of perrhenium acid yields a black precipitate when treated with zinc.

The heptoxide may be formed by burning the metal in oxygen; it condenses from a colorless gas to a yellow liquid at about 350° C. and becomes solid at about 220° C. forming yellow crystals, chiefly in the form of hexagonal plates. After melting the metal or its compounds with caustic alkali, however, rhenates are formed from which can be obtained a reddish yellow oxide considered to have the formula ReO_3. The rhenates of potassium and barium and probably those of other metals are intensely yellow and are much less stable than the corresponding manganates. It is not clearly established in published references whether the oxide ReO_3 has been actually isolated.

A still lower oxide, ReO_2, is formed by the reduction of perrhenium-acid, perrhenates, and the rhenates by hydrogen. By careful reduction with sulphur dioxide, an intermediate blue oxide (between ReO_3 and ReO_2) is obtained. Still another oxide, ReO_4 or Re_2O_8, condensing as a snow-like mass (m.p. about 150-155° C.) may be formed by heating the finely divided metal in oxygen. It is quickly reduced to the heptoxide by ultra-violet light, by heating, or by reducing the pressure; the water solution is readily reduced also and upon evaporation yields Re_2O_7.

Apparently rhenium has various valences, as indicated by the following known oxides: Re_2O_8 (white); Re_2O_7 (yellow); ReO_3 (yellowish-red); various blue and violet oxides of somewhat lower oxidation (Re_3O_8?), and ReO_2 (black). The higher oxides are acid-forming

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5 - Hönigschmid, O, and Sachtleben, R., Revision of the Atomic Weight of Rhenium. Analysis of silver perrhenate: Chem. Abs., vol. 24, Nov. 20, 1930, p. 5546.

6 - Noddack, Ida, Work cited, pp. 629-31.

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and the lower oxides are weakly basic, although the nature of their salts has not yet been investigated.

Of the sulphur compounds the best known is the black disulphide, ReS_2, which is obtained by heating the higher sulphides in a nitrogen atmosphere to about 600° C. Numerous halogen compounds can doubtless be made, and the easily volatile green heptachloride ($ReCl_7$), a brown hexachloride ($ReCl_6$), and a brown bromide of unknown formula have been prepared. Bright-colored oxychlorides are also mentioned but evidently have not been isolated.

Identification and Analysis

Since rhenium yields characteristic lines in the spectrum, these constitute the readiest means of identifying the element. The test is so delicate that the presence of only one part in 10 million may be revealed. Analytically rhenium belongs to the hydrogen sulphide group; in dilute acid solution it yields a black sulphide with H_2S, which is very slightly soluble in alkaline sulphides. In ordinary analysis it is precipitated with molybdenum. In the absence of chromium, manganese, ruthenium, and osmium almost any residual material containing rhenium in amounts of 0.5 per cent or more, forms a yellow-colored melt when fused with caustic alkali. From this melt, alkali rhenates can be extracted with water, forming a colorless solution from which they are not precipitated either by acids or ammonia. This afford an easy means of separation from most associated metals, except arsenic and molybdenum.

Occurrence

Rhenium is undoubtedly an exceedingly rare element and probably is not widely distributed, even in minute amounts, over the surface of the globe. Otherwise, it is reasonable to suppose that the element would not have escaped detection for so many years even after a systematic search was instituted. It is estimated that rhenium constitutes only about one part in a million million of the earth's crust.[7] Originally discovered in tungsten-bearing colombo-tantalite ores and in molybdenite, rhenium was actually found in only 100 out of 1,600 mineral specimens, whose spectra were examined by the discoverers. In exceedingly small amounts, however, the element has been identified in sperrylite and other platinum ores, in magnetic pyrites (pyrrhotite), and in gadolinite--a rare earth mineral containing beryllium and iron in addition to yttrium oxides combined with silica, the formula being written occasionally as $Be_2Fe(YO)_2(SiO_4)_2$.

Norwegian molybdenite, most of it containing less than a thousandth of 1 per cent of rhenium, is the only primary source of rhenium in even potentially commercial quantities. Recent production, however, has been derived from material which apparently has been described as a metallurgical by-product "rich in rhenium," of a certain (unnamed) industry.

History

The history of rhenium is mainly an account of the work of Ida and Walter Noddack, German chemists, who are credited with the discovery of this element (and also masurium) in 1925. In that year they examined 30 complex minerals, in five of which they believed they identified rhenium. From the treatment of 1 kilogram of columbite, they actually obtained

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[7] - U. S. Bureau of Standards, Spectrum of rhenium: Tech. News Bull. 166, Feb., 1931, p. 12.

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about 50 milligrams of a product containing 5 per cent of the two new elements which they named rhenium and masurium. Financed by German scientific bodies the Noddacks were enabled to visit Scandinavian countries and Russia to seek and acquire rhenium-containing minerals, but they failed to find any containing more than 0.001 per cent of the element.

Priority of discovery of element 75 was claimed by J. G. F. Druce who with his co-workers V. Dolejsek and J. Heyrovsky believed that they found it as a frequent impurity in manganese salts. Wilhelm Prandtl working with A. Grimm and W. Franke, however, declared that while even the purest manganese salts contain tungsten, zinc, and cobalt, none of those examined contained the new elements, No. 43 or No. 75.

Extraction and Preparation of Rhenium

A number of processes for recovering rhenium have been patented, but commercial production is now confined to the treatment of a complex sulphide slime obtained as a by-product of an unstated metallurgical process. This slime as it leaves the filter press consists essentially of finely divided reduced metal and sulphides, containing about 12 per cent of molybdenum. After weathering in the air for many months it is leached with water to extract a brownish-green solution containing among other compounds nickel sulphate, a phosphomolybdate of vanadium and nickel, and nickel perrhenate. The nickel and also copper, zinc, and probably cobalt are removed by evaporation supplemented by the addition of measured quantities of ammonium sulphate so as to form double ammonium sulphates. The mother liquor, which is almost black and very thick (density over 2), when treated with more ammonium sulphate yields dark, violet crystals of the ammonium salt of a hetero-poly-acid containing molybdenum, vanadium, and phosphorus.[8] From the pale yellow mother liquor from this fractional crystallization the rhenium is recovered in the form of crystals of potassium perrhenate. As soon as the first crystals of perrhenate appear, the solution is diluted with the mother liquor from a previous crop of crystals and treated with a large excess of potassium chloride. The grey, impure crystals are collected, washed with cold water, and dissolved in dilute sodium (or potassium?) hydroxide, filtering off the insoluble hydroxides. After cooling the filtrate, potassium perrhenate containing only traces of molybdenum and vanadium is obtained, and this can be purified to a product containing 64.6 per cent Re and less than 0.01 per cent impurities by repeating the recrystallization twice.[9]

To obtain rhenium even from this enriched by-product source it is evident that a long series of tedious operations has to be performed; and the cost of the process is further increased by the fact that before the initial extraction with water, the slime has to be kept at the temperature of boiling water (100° C.) and rabbled constantly for at least one month in order to complete the oxidation of the material.

Methods for recovering rhenium by various treatments of molybdenum minerals, some involving fractional sublimation, are outlined in several patents assigned to Siemens & Halske, A. G.; abstracts of these patents will be found in the references listed at the end of this paper. A rhenium-bearing sulphide containing large amounts of molybdenum after reduction with hydrogen followed by heating in a stream of oxygen, yields rhenium in the first sublimate, along with osmium, arsenic, and a little molybdenum. By repeating the process a pure product is obtained, either the white oxide, Re_2O_8, or the yellow oxide, Re_2O_7. The metal is readily reduced from either of these oxides or from the disulphide.

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[8] - Feit, W., Technical preparation of rhenium: Ztschr. angew. Chem., vol. 43, 1930, pp. 459-462; abstract in Chem. and Ind., London, vol. 49, Sept. 5, 1930, p. 822.

[9] - Feit, W., Work cited.

Production and Trade

It is doubtful if rhenium has yet been actually employed for any purely commercial purpose except experimentally. At the end of 1926 the discoverers of rhenium had succeeded in isolating only 2 milligrams of the element; at the end of 1927 this quantity had increased to only 120 milligrams; and in 1928, with the assistance of the Siemens and Halske interests, the Noddacks obtained only 1 gram after treating 700 kilograms of molybdenite. As late as the summer of 1929 only 3 grams, roughly the tenth part of an ounce, had been separated. It was not until 1930, in fact, that rhenium became available in quantities that would permit of its being dispersed among more than two or three laboratories. Evidently the first substantial quantity that appeared in the United States was imported by Charles Hardy of New York, largely for sale to laboratories engaged in scientific or industrial research. The total quantity produced by the end of 1930 was probably in the neighborhood of 300 pounds.

Compared to other rare and newly discovered elements, rhenium is relatively cheap. In "large" quantities it can be bought in the United States for as little as $6 a gram or about $186 a troy ounce, a price that is lower than recent quotations for iridium, a moderately well-known metal. It may be a coincidence that iridium is valued for its hardness, which is one of the properties claimed, though probably in minor degree, for rhenium. In "small" quantities as much as $15 a gram has been asked for the metal in this country.

In Germany, the Vereinigte Chemische Fabriken of Leopoldshall, a subsidiary of the Aschersleben Potash Works, announced[10] that it was in a position to produce perrhenate of potassium, $KReO_4$, at the rate of 400 grams daily or about 265 pounds annually; the price of the compound was quoted at 12 renten marks, about $2.85 per gram gross weight or approximately $4.50 per gram of rhenium content. In April, 1930, Doctor Noddack declared at a meeting of the German Chemical Society that this salt could soon be purchased at 8 marks a gram.

Prospective Uses

As a laboratory chemical, rhenium in the form of potassium perrhenate is recommended for the quantitative determination of potassium. According to researches in the Kaliforschungsanstalt at Berlin, this method is preferable to that involving the perchlorate; the procedure is similar, but less of the reagent is used and the molecular weight of the perrhenate (about 291.8) is more favorable than that of the perchlorate (138.6). The rhenium can be recovered quantitatively by reduction in a stream of hydrogen. According to Hans Tropsch and Robert Kassler, rhenium is capable, like molybdenum and osmium, of catalyzing reduction and hydrogenation processes, such as the production of methane from carbon monoxide and the hydrogenation of the ethylene linkage; this may be done by potassium perrhenate alone, but the addition of copper makes the catalyst more active and effective over longer periods.[11]

A use for the metal is being sought in the radio industry and in the filaments of incandescent electric lamps. The remarkably high melting point and even more remarkably high temperature of vaporization suggest attractive possibilities in these fields, provided the electrical properties, emissivity, and general workability are satisfactory. The hardness of the metal has also been mentioned as a useful property, but data are lacking as to how hard the fused metal actually is. The manipulation of the metal in powder form apparently presents no difficulties at this time, being similar to the technique perfected after long research in connection with the manufacture of tungsten filaments.

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[10] Chimie and Industrie (France), Le Rhenium: Vol. 24, No. 2, Aug., 1930, p. 492.

[11] - Roth, Walter, Potassium Perrhenate Recommended for the Determination of Potassium: Ind. and Eng. Chem. (News Ed.), vol. 8, Nov. 20, 1930, p. 7.

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Hönigschmid, O., and Sachtleben, R. Revision of the atomic weight of rhenium. Analysis of silver perrhenate. Ztschr. anorg. Chem., vol. 191, pp. 309-317, 1930. Chem. Abs., vol. 24, Nov. 20, 1930, p. 5546.

The reduction of ReS_2 is unsuitable for atomic weight determination. Likewise the analysis of the chloride obtained by direct synthesis can not be used on account of a complicated hydrolysis in H_2O. The method adopted was the analysis of $AgReO_4$. By passing H_2 over $KReO_4$ at 400°, a black powder containing the metal and a mixture of oxides is obtained. This was extracted with H_2O, dried in N_2 and ignited in O_2. Large, yellow crystals of Re_2O_7 sublimed. These were dissolved in H_2O to give perrhenic acid from which $AgReO_4$ was precipitated with $AgNO_3$ or Ag_2O. From a solution of $AgReO_4$ in H_2O, AgBr was precipitated with HBr. In seven determinations 51.82860 grams $AgReO_4$ gave 27.17309 grams AgBr, from which the ratio $AgReO_4:AgBr = 1.90735$ and the atomic weight of $Re = 186.31 \pm 0.02$ were obtained.

Noddack, I. and W. Préparation et quelques propriétés chimiques du rhénium. Ztschr. phy. Chem., vol. 125, 1927, pp. 264-274. Bull. Soc. Chim. France, May, 1927, vol. 41-42, No. 5, p. 655.

__________ Oxygen compounds of rhenium. Naturwissenschaften, vol. 17, pp. 93-94, 1929. Chem. Abs., vol. 23, No. 8, April 20, 1929, p. 1833.

A short review of recently determined data on Re. The oxides of this metal are: (1) White oxide, Re_2O_8, formed by continuous oxidation of Re or other oxides in O_2 below 150°. It melts at 150°, going over into yellow oxide; it is soluble in water and in acids and is insoluble in ether. The aqueous solution is weakly acid; it has peroxide qualities (colors Ti and V solutions, discolors $KMnO_4$). (2) Yellow oxide, Re_2O_7, from metal and O_2 above 150°; yellow hexagonal crystals, melting at 200°, is sublimable, boiling at 450°, is undecomposed (in O_2 or N_2), water soluble, hygroscopic, forming a strong acid - perrhenic acid. Salts of the latter were analyzed (Na, NH_4 and Ba); the Na salt melting at 300° undecomposed; heating of the NH_4 or Na salt in H_2 at 400° gives black ReO_2. $Ba(ReO_4)_2$ is soluble, 30 grams per liter of water. Aqueous solutions of Re_2O_7 are easily reduced by Zn, HPO_2, or SO_2 with yellow coloration to (3) red oxide, ReO_3. A solution of black ReO_2 in dilute HNO_3 gives a yellow-red coloration, yellow with NaOH, from which $Ca(OH)_2$ or Ba $(OH)_2$ precipitates bright yellow salts, rhenates, stable only in alkaline solution. ReO_3 in solution goes over on standing or heating into Re_2O_7. (4) Violet and blue oxides formed by the action of SO_2 on dry Re_2O_7 or Re_2O_8; their composition is variable and around Re_3O_8; they are assumed to be compounds of ReO_2 with ReO_3 or Re_2O_7. (5) Black oxide, ReO_2, formed from $NaReO_4$ on heating in H_2; it is reducible in H_2 (800°) to metal.

_________ Oxygen compounds of rhenium. Ztschr. anorg. Chem., vol. 181, pp. 1-37, 1929; cf. Chem. Abs., vol. 23, 1833. Chem. Abs., vol. 23, No. 19, Oct. 10, 1929, pp. 4631-4632.

None of the Re oxides is as well defined as the disulphide (ReS_2). The oxides are therefore not suitable for atomic weight determination. Re is in group VII in the periodic system and its highest oxide is Re_2O_8. This is prepared by passing a stream of cold O_2 over heated solid Re, the oxide being formed as a fine white vapor which is easily condensed. Its density was not determined but is probably about 8.4. It is quickly converted by ultraviolet light, by reduced pressure or by heat into Re_2O_7. Re_2O_8 has a melting point of about 150 to 155°, and is easily soluble in H_2O, from which Re_2O_7 separates on evaporation. The aqueous solution is easily reduced, colors Ti and V solutions yellow, and decolorizes $KMnO_4$. Anhydrous Re_2O_8 is colored violet by SO_2 gas, as is also its solution in concentrated H_2SO_4, a blue precipitate being formed on long standing. This violet solution is decolorized again on heating to boiling. After H_2S is passed into an aqueous solution of Re_2O_8 for some time, S separates, and on warming produces a gray-black sulphide. Re_2O_7 is prepared by heating Re metal in O_2 at a temperature above 150°. It is a bright yellow powder which is easily sublimed, melts at about 220° and has a marked crystalline character. Its density is about 8.2. It is easily soluble in H_2O and alcohol, and very little soluble in Et_2O. Concentrated measurements give values for 86-λ between 366 and 385. An acid is produced on solution in H_2O according to the equation: $Re_2O_7 + H_2O = 2HReO_4$. This dissolves hydrates of Al, Zn, and Fe, as well as metallic Zn or Fe, with evolution of H_2, and is reduced to ReO_3 by Zn and H_2SO_4. Re_2O_7 is reduced to lower oxides by CO or SO_2; H_2 reduces it at 300° to the dioxide and at 800° to metal. Lower oxides are formed by heating it in a vacuum at 300°. Dry Re_2O_7 is converted by dry H_2S into black sulphide. If H_2S is passed into concentrated $HReO_4$, a yellow color is produced, followed by precipitation of the sulphide. If NH_4OH and $(NH_4)_2S_x$ are added to dilute $HReO_4$, nothing is precipitated, but on acidifying with HCl or H_2SO_4 a deep rose is formed and then the gray-black sulphide is precipitated. The reactions of $HReO_4$ with various reagents are given in a table. The salts of $HReO_4$ are colorless, soluble in H_2O, and are more stable than permanganates. Perrhenates of nonvolatile bases can be ignited in O_2 without decomposition. $NaReO_4$ (melting point 200°) is soluble to the extent of 250 grams per liter and crystallizes in hexagonal, colorless tables. $KReO_4$ (melting point 350°, solubility 12.1 grams liter) crystallizes free of H_2O, gives for λ a value of 105 and is reduced to ReO_2 by H_2. NH_4ReO_4 (solubility 120 grams liter) is first reduced to ReO_2 by heating in H_2 at 150° and finally to metallic Re, which is deposited as a mirror on the walls of the reaction flask; $AgNO_3$ gives a white precipitate of $AgReO_4$, soluble in H_2O to the extent of 3.2 grams liter, with $\lambda = 100$. $Ba(ReO_4)_2$ is soluble in H_2O to the extent of 150 grams liter. $Nd(ReO_4)_3$ is prepared by precipitation of the hydrate with NH_4OH and by reaction between this and $HReO_4$. It crystallizes in rose-colored prisms, extremely soluble in H_2O. The trioxide, ReO_3, was not isolated, but its salts are analogous to the manganates. Their solutions in H_2O are bright yellow and are not very stable, decomposing as follows: $3K_2ReO_4 + 2H_2O = 2KReO_4 + ReO_2 + 4KOH$. The violet and blue oxides produced by reduction of higher oxides are probably intermediate between ReO_3 and ReO_2, similar to the lower oxides of W and Mo. They are unstable, particularly the violet oxide. On strong reduction of any O compound of Re, the black dioxide, ReO_2, is formed. It is quickly oxidized to Re_2O_7 in acid solution, but is stable in the presence of alkali. ReO_2 is easily reduced to metal in the absence of H_2O. This reduction is easier than the reduction of the dioxides of Mn, Mo, or W, but more difficult than with Os, placing Re between W and Os. The crystal structure of metallic Re is hexagonal, as is Os, and it can probably be numbered with the Pt metals.

__________ Rhenium from molybdenite. Ztschr. anorg. Chem., vol. 183, p. 352. Foote-Prints, vol. 3, No. 1, 1930, pp. 47-48.

The presence of 0.5 per cent of rhenium can be detected in the absence of chromium, manganese, ruthenium, and osmium by the yellow color of the alkali melt. In ordinary analysis it is precipitated with the molybdenum by hydrogen sulphide. If the sulphides are reduced by hydrogen and heated in oxygen, rhenium is volatilized together with osmium, arsenic, and a part of the molybdenum. By several repetitions of this treatment quite pure white oxide, Re_2O_8, and yellow oxide, Re_2O_7, are obtained.

Noddack, Walter. The chemistry of rhenium. Ztschr. Elktrochem., vol. 34, pp. 627-629, 1928. Chem. Abs., vol. 23, No. 4, Feb. 20, 1929, p. 785.

Reheated in oxygen at 300° forms volatile white Re_2O_7, melting at 26 to 30°, and yellow crystalline ReO_3, melting at 160°. Aqueous solutions of the latter are not affected by common acids and alkalies; Ba $(OH)_2$ and $AgNO_3$ form white precipitates; reducing agents cause a yellow color after a long time in contrast to Mo, W, Ru, and Os; tartaric, oxalic, and phosphoric acids do not prevent the formation of the sulphide. Five reactions distinguish Re from Mo: its yellow-red color with KSCN;K acid xanthate shows only S; NH_4 phosphate and K ferrocyanide are both negative; ReO_3 mixed with MoO_3 sublimes before MoO_3 distils. Re is precipitated quantitatively by H_2S. Three sulphides prepared were Re_2S_7, ReS_3, and ReS_2. $ReCl_6$ forms in Cl. The properties of the Re compounds conform to those of an element between W and Os in the periodic table. In the most stable compounds, Re has a valence of 6 and 7. The ion diameter of Re (Valence lV) is 0.68 A. U.

Roth, Walter (Germany). Potassium perrhenate recommended for the determination of potassium. Ind. Eng. Chem. (News Ed.), vol. 8, No. 22, Nov. 20, 1930, p. 7.

Rhenium was discovered in 1928 by W. and I. Noddack, and in 1929 there were 100 grams in the form of pure rhenium compounds and 100 grams of pure metal in the Physikalisch-Technische Reichsanstalt. The Vereinigte Chemische Fabriken zu Leopoldshall have also recently placed considerable quantities of rhenium, in the form of a very pure potassium perrhenate, upon the market. O. Hönigschmid and R. Sachtleben have used silver perrhenate for an atomic weight determination, and as the result of seven determinations have calculated the atomic weight as Re = 186.31 0.02. Hans Tollert is recommending potassium perrhenate ($KReO_4$) for the determination of potassium. According to researches in the Kaliforschungsanstalt at Berlin, this method of determination is preferable to that as perchlorate; the procedure is similar, but less reagent is used and the molecular weight of the perrhenate (289.4) is more favorable than that of the perchlorate (138.6). The rhenium can be easily recovered quantitatively by reduction in a stream of hydrogen. According to Hans Tropsch and Robert Kassler, rhenium is capable, like molybdenum and osmium, of catalyzing reduction and hydrogenation processes, such as the reduction of carbon monoxide to methane and the hydrogenation of the ethylese linkage - this may be done by potassium perrhenate alone but more actively by a cupriferous catalyst, which is also effective for longer periods of time.

Extraction Methods

Chimie and Industrie. Le Rhénium. Vol. 24, No. 2, Aug., 1930, p. 492.

Druce, J. G. F. Chemistry of dvimanganese, element of atomic number 75. Science Progress, vol. 24, pp. 480-485, 1930. Chem. Abs., vol. 24, No. 10, May 20, 1930, p. 2352.

A description, with bibliography, of the extraction of dvimanganese or rhenium, and of its compounds.

Feit, W. Technical preparation of rhenium. Ztschr. angew. Chem., vol. 43, 1930, pp. 459-462. Chem. and Ind. (London), Brit. Chem. Abs., vol. 49, No. 36, Sept. 5, 1930, p. 822.

An account is given of researches made on the extraction of rhenium from a complex sulphide slime obtained as a by-product in an unstated metallurgical process. The slime had weathered in the air for many months and on extraction with water yielded a brownish-green solution from which nickel and copper sulphates were obtained by evaporation. By the addition of regulated quantities of ammonium sulphate most of the copper, nickel, and zinc were separated as double ammonium sulphates. The almost black mother-liquor had d > 2, and with more ammonium sulphate yielded dark violet crystals of the ammonium salt of a hetero-poly-acid containing molybdenum, vanadium, and phosphorus; the pale yellow mother-liquor yielded crystals of potassium perrhenate on addition of potassium chloride. Large quantities of the slime being worked up as follows: it is heated at 100° with constant rabbling for one month, whereby almost complete oxidation is effected; the residue is extracted with water and the solution evaporated in stages to remove zinc, copper, nickel, and ferrous sulphates. When traces of potassium perrhenate begin to separate the solution is diluted with mother-liquor from a previous crop of crystals and treated with a large excess of potassium chloride. The grey, impure perrhenate is collected, washed with cold water, and dissolved in hot dilute sodium hydroxide; on filtering off the precipitated hydroxides and cooling the solution relatively pure potassium perrhenate is obtained and may be further purified from traces of molybdenum and vanadium by repeating the recrystallization twice. In this way a product with 64.6 per cent Re and less than 0.01 per cent of impurities has been obtained at the rate of 10 kilograms per month at a cost of 10 shillings per gram.

Foote-Prints. Rhenium and masurium. Vol. 3, No. 1, 1930, p. 48.

The new elements are isolated by sublimation from materials containing them such as platinum ores, gadolinite, sperrylite, and molybdenite. A sulphide containing molybdenum 70 per cent, arsenic 22 per cent, and rhenium 0.2 per cent may be reduced by hydrogen and then heated in a stream of oxygen. The first sublimate contains the rhenium.

Noddack, I. and W. Preparation of one gram of rhenium. Ztschr anorg. Chem., vol. 183, pp. 358-375, 1929. Chem. Abs., vol. 24, No. 3, Feb. 10, 1930, pp. 560-561.

Norwegian molybdenite containing 2 to 4 times 10^{-6} per cent Re was the raw material. The presence of Re is detected, and its amount estimated by the arc and spark spectra. If the content of Re is 0.5 per cent or more it can be detected in the absence of Cr, Mn, Ru, and Os by the yellow color of the alkali melt. The formation of a white, easily volatile peroxide, Re_2O_8, by gentle ignition in O_2 is characteristic. This peroxide turns yellow on heating to 160° and gives a black sulphide with H_2S. In ordinary analysis Re is precipitated with Mo by H_2S. If such sulphides are reduced by H_2 and the product taken up in NaOH and an alkaline nitrate, Re goes into solution with Mo, W, As, Ge, Ru, Os, Sb, V, and Pb and is again precipitated with these as sulphides. If sufficient Re is present, the reduced metallic mixture can be heated in O_2, the Re being volatilized together with Os, As, and a small part of the Mo. Several methods of separation of Re from Mo are described. The authors treated the molybdenite as follows: It was ground to pass a 200-mesh sieve, and to 5 kilograms of the powder, 25 liters of HNO_3 (d. 1.40) is slowly added. 660 kilograms of the material must be treated in this manner. The acid solution is made definitely alkaline with 25 per cent NH_4OH and the precipitate allowed to settle, after which it is washed with H_2O filtered and dried at 60°. Analysis shows that it still contains about 50per cent MoS_2. The dry material is ground and sieved and again treated with HNO_3 and precipitated with NH_4OH. The ammoniacal solutions are treated with Na_2HPO_4 (20% solution) and HNO_3 until precipitation of Mo is complete. After filtration the filtrate now contains all of the Re and any Mo not precipitated. It is treated with $(NH_4)_2S$ and the mixed sulphides of Re and Mo are washed with H_2O and dried at 60°. They are then dissolved in concentrated HNO_3, the solution is diluted with H_2O and treated with NH_4OH. This is again precipitated with Na_2HPO_4 and HNO_3 to remove more Mo. The filtrate is again precipitated with $(NH_4)_2S$, giving a mixed sulphide containing an increasing quantity of Re as well as an accumulation of impurities such as Ni, Cu, Co, Fe, Pt, and V. Ni, Cu, Co, and Fe are removed by reducing in H_2 at 1000°, the reduced product being treated with fused NaOH + $NaNO_3$ in an Ag crucible, the melt taken up in H_2O and filtered. The solution is precipitated with $(NH_4)_2S$ in the presence of H_2SO_4, the sulphide precipitate is reduced with H_2 and the product found to contain 68.5 per cent Mo, 23 per cent V, 3 per cent As, 1.5 per cent Pt, 1.5 per cent Pb, 0.8 per cent Ir, and 1.9 per cent Re. This material is heated in a current of O_2, Re being volatilized as white Re_2O_8 and yellow Re_2O_7. The product is dissolved in HNO_3 precipitated as sulphide, reduced and found to contain 93.5 per cent Re, 5 per cent Mo, 1.2 per cent As, 0.2 per cent Pb and 0.05 per cent Ni. This is ignited for a long time in H_2 at 1000°, freed from As by heating in O_2 at 150°, finally volatilized again, reduced, resublimed, and treated in this manner until quite pure Re is obtained. Its purity is tested spectroscopically. No impurities were found in greater amount than 2×10^{-4}.

Siemens and Halske, A. G. Extraction of rhenium concentrations. British patent 332,627, Nov. 22, 1928. Metals and Alloys, vol. 1, No. 16, Oct., 1930, p. 808.

_________ (Walter Noddack and Ida Noddack, inventors). Rhenium; masurium. German Patent 483,495, June 19, 1925. Chem. Abs., vol. 24, No. 5, March 10, 1930, p. 1188.

Rhenium and masurium (the "ekamanganeses" of atomic nos. 43 and 75), are concentrated or isolated from materials containing them by sublimation. Suitable initial materials are Pt ores, gadolinite, sperryite and molybdenite. Pretreatment of the initial materials may be necessary. Thus, a sulphide mixture, the metal content of which comprises Mo 70, As 22, Re 0.2, and other specified metals 7.8 per cent, may be reduced in H and then gently heated in a stream of O. The first portion of the sublimate is enriched in Re, and further concentration may be effected by resubliming. The metal chlorides also may be fractionally sublimed.

_________ Rhenium compounds. British patent 317,035, Aug. 9, 1928. Chem. Abs., vol. 24, No. 8, April 20, 1930, p. 1943.

Rhenium is extracted from Mo ores or compounds by dissolving the Mo as MoO_3 in HNO_3 and precipitating Mo as phosphomolybdate with NH_4NO_3 and H_3PO_4 or a phosphate, leaving the rhenium and some Mo in solution. Rhenium and Mo are precipitated together from this solution by H_2S and the precipitate is redissolved in HNO_3; these steps are repeated in sequence until the solution may contain 0.5 to 2.0 per cent of rhenium with respect to the Mo still present. Rhenium is then recovered, as by fractional distillation. Cf. Chem. Abs., vol. 24, p. 1188.

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__________ Process for obtaining rhenium. British patent 317,035. Aug. 9, 1928. Chem. Age, vol. 23, No. 581, Aug. 16, 1930, p. 149.

__________ Extracting rhenium. International Convention date, Nov. 22, 1928. British patent 332,627. Chem. Age, vol. 23, No. 587, Sept. 27, 1930, p. 292.

Minerals such as columbite, gadolinite, or magnetic pyrites, are dissolved in hydrochloric acid, and the sulphides are precipitated with hydrogen sulphide. In the case of magnetic pyrites containing 0.00001 per cent of rhenium, the precipitate may contain arsenic, molybdenum and rhenium only. The sulphides are then dissolved in nitric acid, and constituents other than rhenium precipitated with ammonium nitrate and phosphoric acid. This is repeated several times, and when the rhenium is sufficiently concentrated it may be recovered by fractional sublimation, reduction of the sulphide concentrate by hydrogen, oxidation in oxygen, reduction, fractional volatilization, and reoxidation.

__________ Production of rhenium. British patent 317,035. German patent, Aug. 9, 1928. Chem. and Ind. (London), vol. 49, No. 44, Oct. 31, 1930, p. 994.

Molybdenite is dissolved in nitric acid and the solution treated with ammonium nitrate and phosphate to remove the greater part of the molybdenum as ammonium phosphomolybdate. The filtrate is treated with hydrogen sulphide, the mixed molybdenum rhenium sulphide redissolved in nitric acid, and the phosphate treatment repeated. This procedure, after several repetitions, affords a sulphide precipitate from which a rhenium concentrate may be obtained by fractional sublimation in air.

__________ Recent patents published. German patent 6,421 of 1929 (317,035). Min. Mag. (London), vol. 43, No. 4, Oct., 1930, p. 254.

Rhenium is prepared from natural molybdenum minerals, the molybdenum being dissolved in nitric acid and precipitated by phosphoric acid, leaving the rhenium in solution.

General

Baxter, Gregory P. Thirty-fifth annual report of the committee on atomic weights. Determinations published during 1928. Jour. Am. Chem. Soc., vol. 51, pp. 647-654, 1929. Chem. Abs., vol. 23, No. 9, May 10, 1929, p. 2080.

The work done during 1928 on K, Ti, Cu, Ca, Ba, Ag, Ce, Er, Re, Pb, and U is reviewed. The table of atomic weights for 1929 is given in which changes from the 1928 table are made for H, P, S, Ba, Ce, Er, K, Ra, Th, and U.

Bodenstein, M., Hahn, O., Hönigschmid, O., and Meyer, R. J. Report of the German Atomic Weight Commission. Ber. Dent. Chem. Gesell., vol. 63B, 1930, pp. 1-24; cf. Chem. Abs., vol. 22, p. 1066. Chem. Abs., vol. 24, No. 8, April 20, 1930, p. 1774.

The atomic weight of Re is taken as 188.7 and the atomic weight of O written 16.0000. A summary of important work on atomic weights published since the last report discusses the elements, H, A, C, S, P, Cu, Hg, B, Pb from Act, N, As, Sb, Cl, Re, and Ni. Work on isotopes is reviewed, including O, C, Ra, Pa and Pb.

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Canadian Mining Journal. Rare metals and prospecting. Vol. 51, No. 20, May 16, 1930, pp. 473-474.

Chemical Age (London). Rhenium metal and its compounds. (Some recent German research). Vol. 22, No. 562, pp. 22-23, April 5, 1930.

Abstract of a summary of available data by the Noddacks in Die Metallböerse, March 19, 1930.

Chemistry and Industry (London). Rhenium available as potassium rhenate. Vol. 49, No. 17, April 25, 1930, p. 348.

Dolejsek, V., Druce, G., and Heyrovsky, J. The occurrence of dvimanganese in manganese salts Nature, vol. 117, Jan. 30, 1926, p. 159.

The presence of element 75 is indicated by both chemical and electrochemical methods in manganese salts. The authors consider that dvimanganese is most appropriate name for new element.

Dolejsek, V., and Heyrovsky, J. The occurrence of dvimanganese (At. No. 75) in manganese salts. Nature, vol. 116, Nov. 28, 1925, pp. 782-783.

Druce, J. G. F. The discovery of eka and dvi-manganese (masurium and rhenium). Chem. Weekblad, vol. 23, 1926, pp. 318-320. Chem. Abs., vol. 20, 1926, p. 3127. Bull. Soc. Chim. France, Jan., 1927, p. 37.

_________ Dvimanganese. Continental Met. and Chem. Eng., vol. 1, 1926, pp. 111-112. Chem. Abs., vol. 21, April 10, 1927, p. 1035.

Druce claims to have detected element 75 in pyrolusite, and attributes the catalytic action of MnO_2 on $KClO_3$ to the small quantities of this element present in the Mn. He concluded with a defense against the attack of the Noddacks and with the statement that 1 per cent of element 75 has been detected by X-ray spectrograms of his concentrates.

_________ Recent work on dvimanganese; a reply. Chem. Weekblad, vol. 23, pp. 497-498, 1926 (In English). Chem. Abs., vol. 21, Mch. 10, 1927, p. 677.

A reply to criticisms of Prandtl (Chem. Abs., vol. 21, p. 16) and of W. and I. Noddack (Metallboerse, vol. 16, 1926, p. 2129). Druce maintains his previous views (Chem. Abs., vol. 20, pp. 2101, 3127).

Goldschmidt, V. M. The crystal structure of rhenium. Naturwissenschaften, vol. 17, pp. 134-135, 1929. Chem. Abs., vol. 23, No. 10, May 20, 1929, p. 2335.

Black rhenium powder (10.9 mg. with 0.3% Mo) has hexagonal structure with close packing, a = 2.752 ± 0.001 A. U., c = 4.440 ± 0.002 A. U.; it is similar in this respect to Os. The atom radius of Re is between those of W and Os, 1.371 A. U. By using Noddacks atomic weight of 188.71 ± 0.25, a value of 21.33 for the density of the experimental material is calculated; for pure Re is calculated 21.40 ± 0.06 in agreement with measured values.

_________ The crystal structure, lattice constants, and density of rhenium. Ztschr. Phys. Chem., Abt. B, vol. 2, 1929, pp. 244-252. Chem. Abs., vol. 24, No. 9, May 10, 1930, p. 2026.

The crystal structure of Re was determined by the Debye-Scherrer method. A typically hexagonal close-packed lattice pattern was found. Rock salt and MgO were used as standards. The cell dimensions are: a = 2.752 ± 0.001 A. U.; c = 4.448 ± 0.002 A. U.; c/a = 1.616 ± 0.001. d = 21.33 ± 0.06 for the specimen examined (containing 0.3% Mo); pure Re should have d = 21.40 = 0.06. The atomic radii of the elements 72-76 (Hf to Au), in twelvefold coordination, are: Hf, 1.585 A. U.; Ta, 1.461 A. U.; W, 1.408 A. U.; Re, 1.371 A. U.; Os, 1.336 A. U.; Ir, 1.352 A. U.; Pt, 1.380 A. U.; Au, 1.439 A. U.

Heyrovsky, J., and Druce, G. The occurrence of dvimanganese (At. No. 75) in manganese salts. Nature, vol. 117, Jan. 2, 1926, p. 16. Bull. Soc. Chim. France, April, 1926, p. 414.

Reply of Heyrovsky and Druce to the criticism of M. A. N. Campbell.

Metal Industry (London). The capture of the elements. Vol. 36, No. 17, April 25, 1930, pp. 447-448.

Mining Journal (London). Rare metals. Vol. 168, No. 4936, March 29, 1930, p. 2.

Noddack, W., and Tacke, -. Two new elements of the manganese group. Nature, vol. 116, July 11, 1925, pp. 54-55.

Résumé of authors' work on elements 43 and 75. By treating they obtained one kilogram of columbite, 0.050 grams of product containing 5 per cent of elements 43 and 75. X-ray examination showed existence of three rays of the K-series for element 43, and five rays of the L-series for element 75. The authors affirm the presence of the new elements in the columbite and name them masurium (Ma) and rhenium (Re), respectively.

Noddack, Ida. Some physical constants of rhenium. Ztschr. Elektrochem., vol. 34, 1928, pp. 629-631. Chem. Abs., vol. 23, No. 7, April 10, 1929, p. 1537.

Briefly surveys the physical properties of Re. A spectrogram and table of wave lengths of the lines of the L-series of the Röntgen spectrum, as determined by Beuthe, are given. The spark and arc spectra also are qualitatively well known, and several hundred lines in them are known certainly to belong to Re. The ultimate lines of the optical spectrum, especially the triplet at 3640 A. U., serve to detect Re in concentration down to 10^{-7}, and greatly facilitate the examination of Re-containing minerals. The density of the black metal powder formed by the reduction of ReS_2 in H_2 is 10.4. Re fused in the C arc is white, similar in appearance to Pt, and stable in air. When melted on the anticathode, Re formed bright spheres 0.05 to 0.01 millimeters in diameter, having a density of about 20. The melting point of Re is very high, possibly higher than that of W. There are indications that its boiling point is above that of W and C. Its specific heat, 0 to 20°, is 0.0346. Atomic weights have been determined by analysis of Re_2O_3 and Re_2O_7, but the values are probably too high because of contamination by lower oxides. The most reliable figure for the atomic weight at present is 188.71 ± 0.25, determined by the reduction of ReS_2 to Re in a stream H_2 at about 1000°. Details of this procedure are given. The analysis of $ReCl_6$ may furnish the best method for atomic weight determination as soon as the properties and stability of the different Re chlorides have been studied more thoroughly.

Noddack, Ida and Walter. Rhenium. Metallboerse, vol. 20, 1930, pp. 621-622; Cf. Chem. Abs., vol. 23, p. 4631. Chem. Abs., vol. 24, Aug. 20, 1930, p. 3959.

After five years work the existence of Re may now be considered proved; 1,600 minerals from all over the world have been examined and Re was found in 100 of them. From 2 milligrams of Re in 1925 the amount available had grown to 3 grams in 1929, and in 1930 several hundred grams were available. No mineral has been found to contain more than 0.001 per cent of Re. The physical and chemical properties of Re are summarized, and its resemblance to W and Os is pointed out. The advent of Re as a technical product within a year is probable.

__________ Recent investigations of the elements masurium and rhenium. Continental Met. and Chem. Eng., Nov. 4, 1926, p. 109.

A description of the method by which the authors proved the existence of the new elements 43 (Ma) and 75 (Re). Norwegian columbite is the raw material used. Abstract from Jour. Chem., Met. and Min. Soc. South Africa, vol. 27, April, 1927, p. 238.

Prandtl, Wilhelm. The search for the manganese homologs Nos. 43 and 75. Ztschr. angew. Chem., vol. 39, pp. 1049-1051 (Report of work with A. Grimm and W. Franke). Chem. Abs., vol. 21, Jan. 10, 1927, p. 16.

Four minerals, manganotantalite from British Namaqualand, tantalite from Finland, gadolinite from South Norway and wolframite from Zinnwald, were chemically treated and analyzed by X-rays without result. Later niobite from South Norway and columbite frqm Finland were similarly tested in vain. About 1 gram of each material was used. Noddack and Tacke (cf. Chem. Abs., vol. 19, p. 3391) sent P 3½ mg. of black material said to contain Re (75) to the extent of 0.8 to 1 per cent. None was found. The two principal (L) lines of Re are very close to the principal (K) line of Zn and to a weaker W line (LB_8).

All commercial Mn salts, even the purest, contain W, Zn, and Co, but no elements 43 or 75. The green color (C. A. 20, 3127) of the solution is due to Co. It will only be certain that these elements are really discovered if they can be found reproducibly in Zn and W free preparations.

Schacherl, Fr. The homologs of manganese. Chem. Listy, vol. 23, pp. 632-635, 1929. Chem.

Abs., vol. 24, No. 20, Oct. 20, 1930, p. 4996.

The elements Ma and Re (At. nos. 43 and 75) belong to the Mn group. They may be searched for in Mn, Pt, and W ores. The ReS_2 was prepared from gadolinite and columbite; it served for preparing the oxides and the free metal. The melting point was higher than that of W. By reducing the ReS_2, the atomic weight was found to be 188.7 ± 0.25. With O the compounds are ReO_2, Re_2O_8, ReO_2, and Re_2O_7, which form salts of the type M_2ReO_4 and $MReO_4$. The sulphides Re_2S_7, Re S and ReS_2 are black; only the last one is stable. In a current of Cl, two compounds, $ReCl_6$ (brown) and $ReCl_7$ (grass green), form. Compounds with Br and I also form.

Siemens and Halske, A.-G. Catalyst. French patent, 682,446, Sept. 30, 1929. Chem. Abs., vol. 24, No. 17, Sept. 10, 1930, p. 4362.

Ekamanganeses, i. e., elements corresponding to the numbers 43 (masurium) and 75 (rhenium), and their compounds are used as catalysts, e.g., for the oxidation of SO_2 to SO_3, for converting $PhNH_2$ to aniline black and for chlorinating processes. Examples are given which use metallic rhenium and rhenium heptoxide.

Spectrum

Berg, O. The Röntgen spectrum of element 75. Physikal Ztschr., vol. 28, 1927, pp. 864-866. Chem. Abs., vol. 22, No. 6, March 20, 1928, p. 909.

On account of the critism directed against the first Röntgen-ray evidence for element 75, additional evidence of the same nature is now presented. Spectrograms showing four lines, α, α_2, β, β_2, of the L-series of element 75 are reproduced. These were obtained from preparations derived from Norwegian gadolinite; it is estimated that Re content of these preparations is about 2 per cent.

Beuthe, H. The L-series of rhenium. Physikal Ztschr., vol. 46, 1928, pp. 873-877. Chem. Abs., vol. 22, No. 8, April 20, 1928, p. 1276.

A Bragg Röntgen spectrograph is used to study the spectrum of the L-series of Re obtained from a material containing 80 per cent Re, 15 per cent Mo and small quantities of As, Se and Ni. The wave lengths of 16 L-series lines of Re (1023.5 to 1627.3 X. U.) are measured relative to impurity lines.

__________ Further Röntgen spectroscopy measurements in the L and M series of rhenium. Physikal Ztschr., vol. 50, 1928, pp. 762-768; cf. Chem. Abs., vol. 22, p. 1276. Chem. Abs., vol. 23, No. 1, Jan. 10, 1929, p. 30.

The weaker lines of the L series of Re, the L-absorption bands and the strongest lines of the M-series are measured and the corresponding terms values are calculated. The determination of the wave lengths of weaker lines forms an extension of the earlier work on the L-series of Re (cf. Chem. Abs., vol. 22, p. 1276). The wave lengths of 25 L-series lines ranging from 991.0 to 1627.3 X. U. are tabulated; the L-absorption limits are measured at 1173.8, 1034.0, and 987.1 X. U., and four M-series lines are measured at 6708, 6692, 6491 and 5873 X. U.

Lindberg, E. Measurements of the M-series in the Röntgen spectra of the elements from uranium to gadolinium. Physikal Ztschr., vol. 50, 1928, pp. 82-96. Chem. Abs., vol. 23, No. 1, Jan. 10, 1929, p. 32.

A careful study has been made of the M-series of the elements from U (92) to Gd (66), including Re (75) and Hf (72). A Siegbahn precision vacuum spectrometer was used in the work, and the results cover the wave-length interval from 2.5 to 11.5 A. U. The wave-length measurements for each element are listed in comprehensive tables, as are also the values of V/R and $\sqrt{V/R}$ derived from them.

Wennerlöf, Ina. Precision measurements in the L-series of the new element 75, rhenium. Physikal Ztschr., vol. 47, 1928, pp. 422-425. Chem. Abs., vol. 22, No. 11, June 10, 1928, p. 1878.

On a preparation containing 5 per cent Re and 92 per cent Mo, obtained in the work of I. and W. Noddack (Chem. Abs., vol. 21, p. 1570), accurate wave-length measurements were made for the three strongest X-ray lines of Re with the following results: $L\alpha_1$ 1429.88, $L\beta_1$ 1236.04 $L\beta_2$ 1204.1 x-units. These values are in good agreement with those obtained by interpolation from the $\sqrt{V/R}$ values of neighboring elements, and leave no doubt as to the actual presence of element 75.